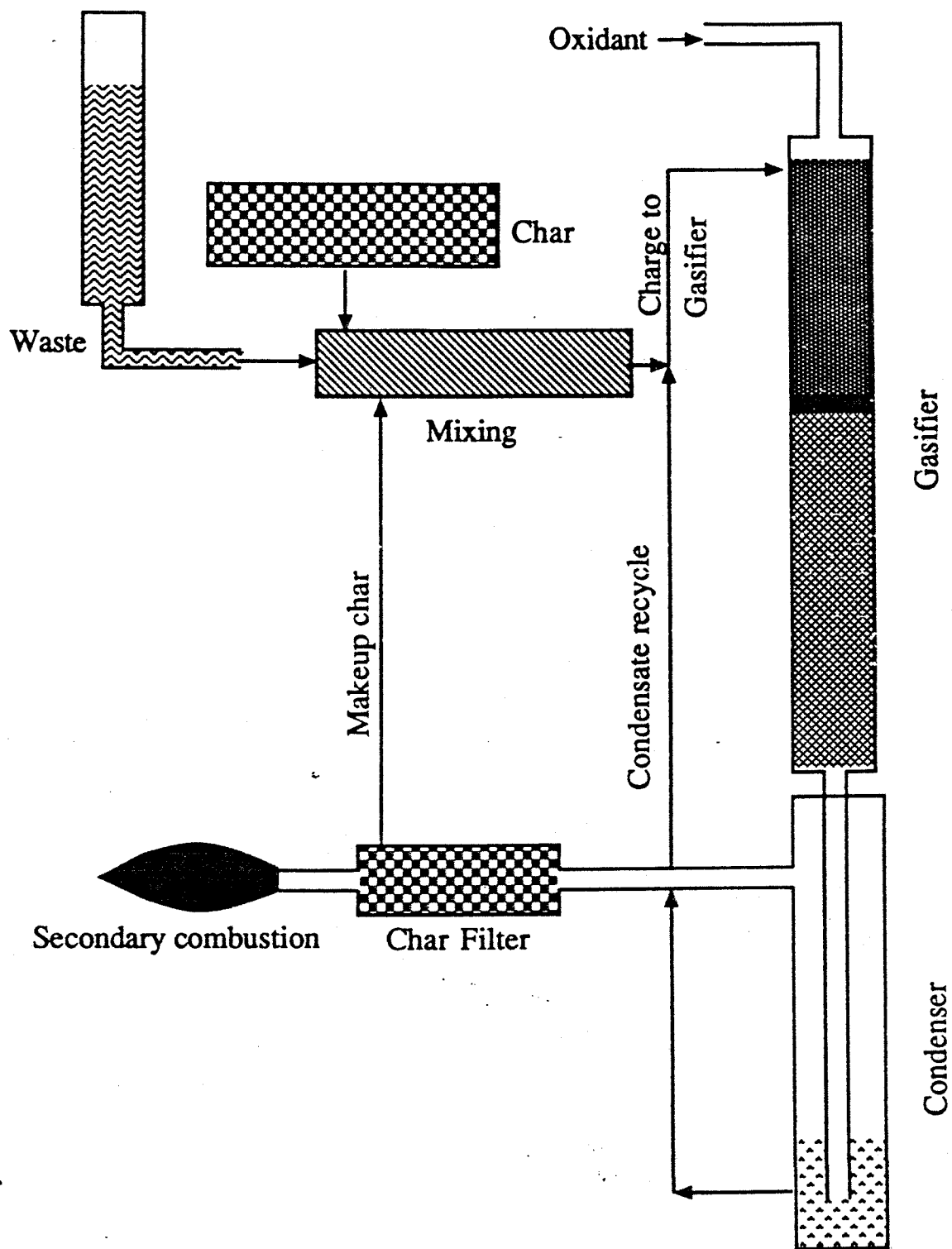# REVERSE-BURN GASIFICATION OF HAZARDOUS WASTES

APPLICATION TO TREATMENT OF REFRACTORY ORGANIC WASTE, CONTAMINATED SOIL, SEWAGE SLUDGE, MIXED RADIOACTIVE WASTES AND SPENT ACTIVATED CARBON.

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August 1991

The ChemChar Process for Treatment of Hazardous Wastes

Oxidant

Char

Waste

Mixing

Charge to Gasifier

Gasifier

Makeup char

Condensate recycle

Secondary combustion

Char Filter

Condenser

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Reverse-Burn Gasification of Hazardous Wastes: Application to Treatment of Refractory Organic Waste, Contaminated Soil, Sewage Sludge, Mixed Radioactive Wastes and Spent Activated Carbon

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Abstract

A unique reverse-burn gasification process employing secondary combustion of the product gases is described. The process has been applied to a variety of hazardous and non-hazardous wastes, including refractory organic wastes, such as wastes containing both PCBs and heavy metals; contaminated soil; sewage sludge; mixed wastes containing both organic substances and radioactive materials; and spent activated carbon, which can be regenerated and re-activated by reverse-burn gasification. The process is especially useful in destroying hazardous wastes because of the unique characteristics of reverse-burn gasification, which is particularly effective for dehydrohalogenating organohalide compounds without producing undesirable byproducts, such as dioxins, and in retaining heavy metals and acid gases, such as hydrogen chloride produced in the destruction of organohalides. With second-stage combustion of the product gas, destruction/removal efficiency of greater than 99.9999% ("six nines") is readily achieved.

The Reverse-Burn Gasification Process

Reverse-burn gasification is a thermochemical process that offers a number of advantages over conventional incineration for the treatment of a variety of waste materials. Patented as the ChemChar Process,[1,2] reverse-burn gasification can treat wastes in the forms of solids, liquids, sludges, and soils.[3] Waste constituents are destroyed by conversion to a combustible gas and to a dry, inert, carbonaceous solid which is either non-hazardous or can be readily mixed with cement to prevent leaching of the radioactive, toxic, or heavy metal constituents that are retained in the char residue or ash. In this way, reverse-burn gasification can be a very effective method for treating organic waste sludges containing heavy metals[4] and mixed wastes consisting of hazardous chemicals contaminated with radioactive substances.[5]

As with any gasification waste treatment process, reverse-burn gasification offers inherent advantages in the areas of destruction efficiency and emissions control. This is because, instead of an exhaust gas that must be treated to control emissions, gasification produces a combustible gas that is burned. Trace levels of contaminants are destroyed in burning the gas, and a catalyst may be employed, if necessary. Therefore, rather than attempting to burn wastes consisting of oily sludges, semisolids, and similar refractory materials for which efficient combustion is difficult and the use of a catalyst impossible, two-stage waste destruction by gasification followed by combustion of the gas product enables the combustion step to be carried out in the optimum configuration, leading to facile destruction of wastes at levels exceeding even 99.9999%.

Figure 1 shows a diagram of the batch mode version of the reactor used for reverse-burn gasification (a continuous-feed version is under development). For gasification the reactor is charged with a granular solid containing combustible matter. The combustible material may consist of carbon or of organic matter bound to the solid. Water, which aids gasification and provides a source of hydrogen for waste-destroying reactions, such as dehydrohalogenation, may be present on the solid or introduced as steam into the oxidant stream. Oxygen, oxygen-enriched air, or compressed air is passed through the reactor and a flame front is
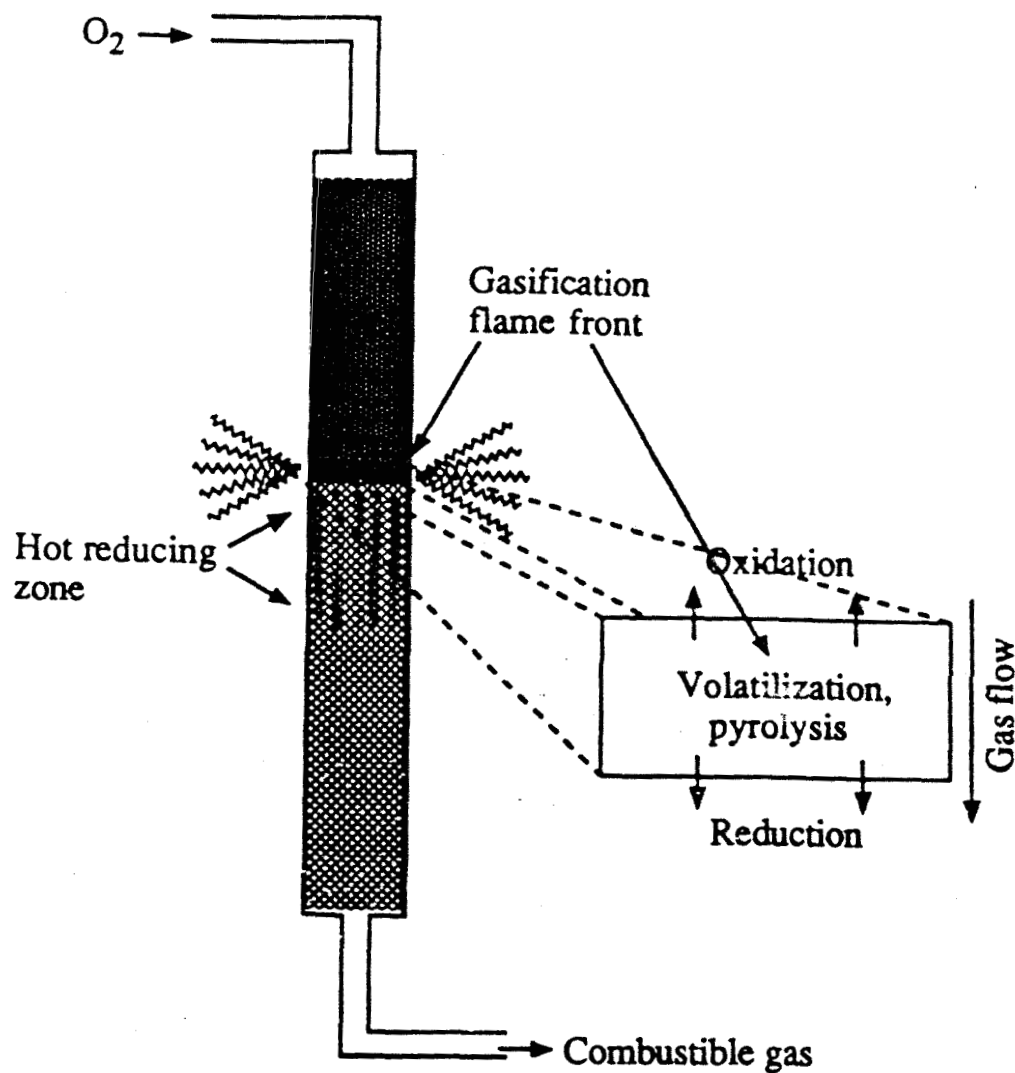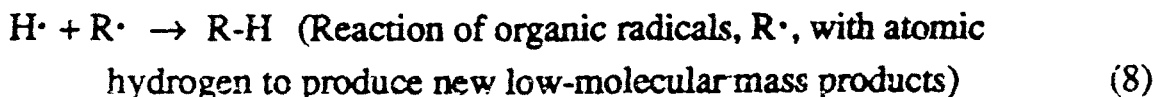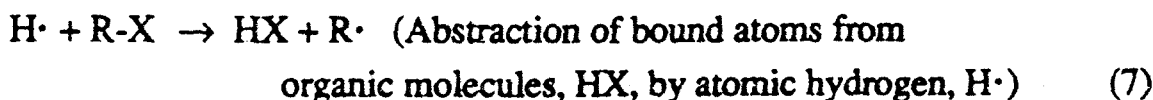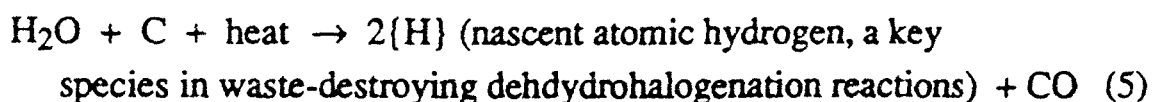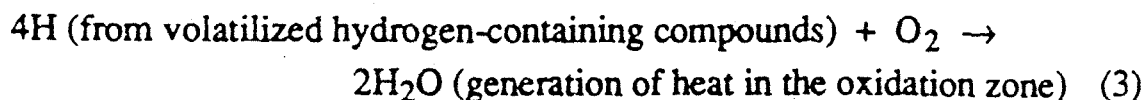
Figure 1. Schematic of gasifier in reverse-burn gasification. The gasification zone is shown in the enlarged portion of the figure. The gasification zone moves in a direction counter to the gas flow; immediately downstream from it is a non-incandescent hot reducing zone. The upper portion of the flame front is oxidizing, the lower portion reducing. Gases flow downward through the column. These consist of cool oxidant upstream from the gasification zone and hot reducing gases downstream.

initiated by heating the downstream end of the plug of solid material in the reactor. The gasification flame front at a temperature in excess of 1200°C moves in a direction opposite to the flow of gas. A portion—typically 10%—of the material in the reactor is gasified in the flame front. Gasification occurs in three regions of

the gasification zone shown in an enlarged view in Figure 1. In a simplified sense these reactions are the following:

$$C + O_2 \rightarrow CO_2 \text{ (generation of heat in the oxidation zone)} \tag{1}$$

$$2C + O_2 \rightarrow 2CO \text{ (generation of heat and combustible}$$
$$\text{gas in the oxidation zone)} \tag{2}$$

$$4H \text{ (from volatilized hydrogen-containing compounds)} + O_2 \rightarrow$$
$$2H_2O \text{ (generation of heat in the oxidation zone)} \tag{3}$$

$$CO_2 + C + \text{heat} \rightarrow 2CO \text{ (generation of combustible gas)} \tag{4}$$

$$H_2O + C + \text{heat} \rightarrow 2\{H\} \text{ (nascent atomic hydrogen, a key}$$
$$\text{species in waste-destroying dehdydrohalogenation reactions)} + CO \tag{5}$$

$$2\{H\} \rightarrow H_2 \tag{6}$$

$$H \cdot + R\text{-}X \rightarrow HX + R \cdot \text{ (Abstraction of bound atoms from}$$
$$\text{organic molecules, HX, by atomic hydrogen, } H \cdot) \tag{7}$$
$$H \cdot + R \cdot \rightarrow R\text{-}H \text{ (Reaction of organic radicals, } R \cdot, \text{ with atomic}$$
$$\text{hydrogen to produce new low-molecular mass products)} \tag{8}$$

As reverse-burn gasification occurs with movement of the flame front counter to the oxidant flow, a combustible synthesis gas consisting of H_2, CO, CO_2, H_2O vapor, and trace volatile organic constituents is evolved from the gasifier. Reverse-burn gasification of a carbonaceous material, such as coal, leaves a solid carbon product from which water and volatile organic matter have been removed. The carbonaceous solid residue retains heavy metals, and, when the parent solid material is alkaline, acid gases, such as HCl. If the flame front is not extinguished by cutting off the oxidant flow when it reaches the top of the solids reactor charge, or when it is initiated at the top of the reactor charge, forward burn gasification occurs as the flame front travels in the same direction as the oxidant flow and consumes all combustible material.

The chemical environments in the flame front and the hot reducing zone immediately downstream from it determine the characteristics of reverse-burn gasi-

fication that are crucial to its success as a waste treatment process. These characteristics are covered in greater detail in the discussion section of this paper.

TRB Char

A key constituent of the ChemChar waste treatment process discussed in this chapter is the granular char matrix on which many of the waste materials studied, such as sludges, are held and immobilized for gasification. This char is prepared by gasification of subbituminous coal in the reactor shown in Figure 1.[6] The subbituminous coal chosen is a non-swelling, low-sulfur, high-alkalinity fuel that pro-
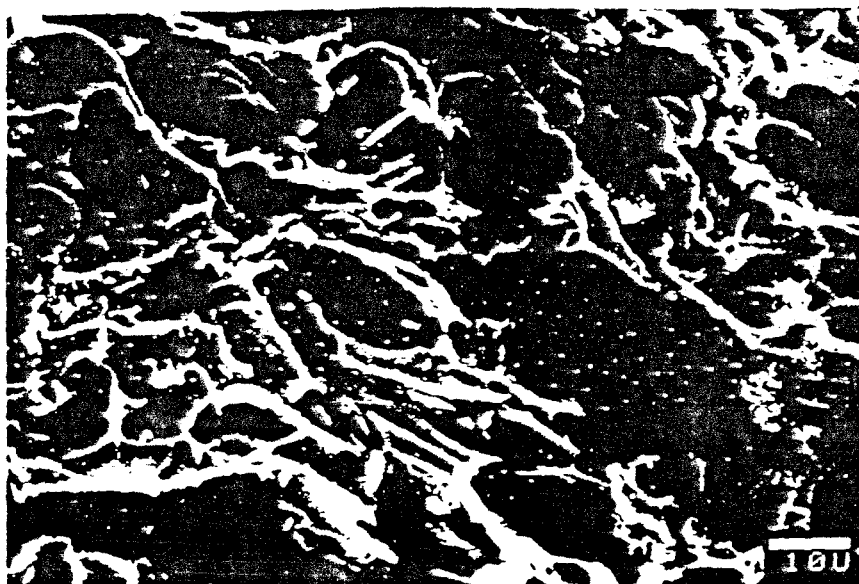

Figure 2. Electron micrograph of TRB char generated by triple-reverse-burn gasification of subbituminous coal and used as a support matrix for waste gasification. The macroporous structure of the char is clearly shown.

duces a char with the characteristics needed for waste treatment. Prepared by three consecutive reverse-burn gasification runs, it is called triple-reverse-burn (TRB) char.[7] As shown by the electron micrograph in Figure 2, TRB char is a highly porous material with macropores of the order of several μm in size, which enable it to absorb as much as its own mass of liquids and sludges. Because of the capillary action of the macropores, TRB char also serves as a drying agent for some kinds of

sludges, rejecting water and retaining organic and non-volatile components. In contrast to the starting materials immobilized on it, the waste-laden char is a dry, granular, readily handled material. It is a low grade activated carbon with a surface area of approximately 100–200 m^2/g.

TRB char loaded with wastes provides a support with relatively uniform physical and chemical properties for destruction of wastes by gasification. The granular medium holds the waste constituents and allows for uniform passage of gases. The carbonaceous matrix provides a chemically reducing medium and a source of hydrogen required for dehydrohalogenation (Reaction 7) generated by Reaction 5.

As a support material and matrix for waste gasification, TRB char offers the following advantages:

- TRB char is inexpensive to produce.

- It sorbs a wide variety of substances, both organic and inorganic.

- The mechanically stable nature of the char and its high volume of relatively large pores provides an ideal physical matrix for mixing, drying and retention of sludge wastes.

- The carbonaceous surface of the char provides a matrix on which thermochemical reactions can occur under controlled conditions.

Waste Treatment by Reverse-Burn Gasification

Gasification destruction of wastes, which are often immobilized on a char matrix, is accomplished with the gasification reactor shown in Figure 1. The waste treatment system is shown in the schematic diagram in Figure 3 and involves the following steps:

- Mixing TRB char with wastes: Although some kinds of wastes, such as granular soil containing 5-10% combustible matter, can be gasified without mixing with char, most wastes are mixed with char for subsequent gasification. Liquid wastes can be sorbed directly onto the char surface. Aqueous wastes can be filtered through a bed of char to
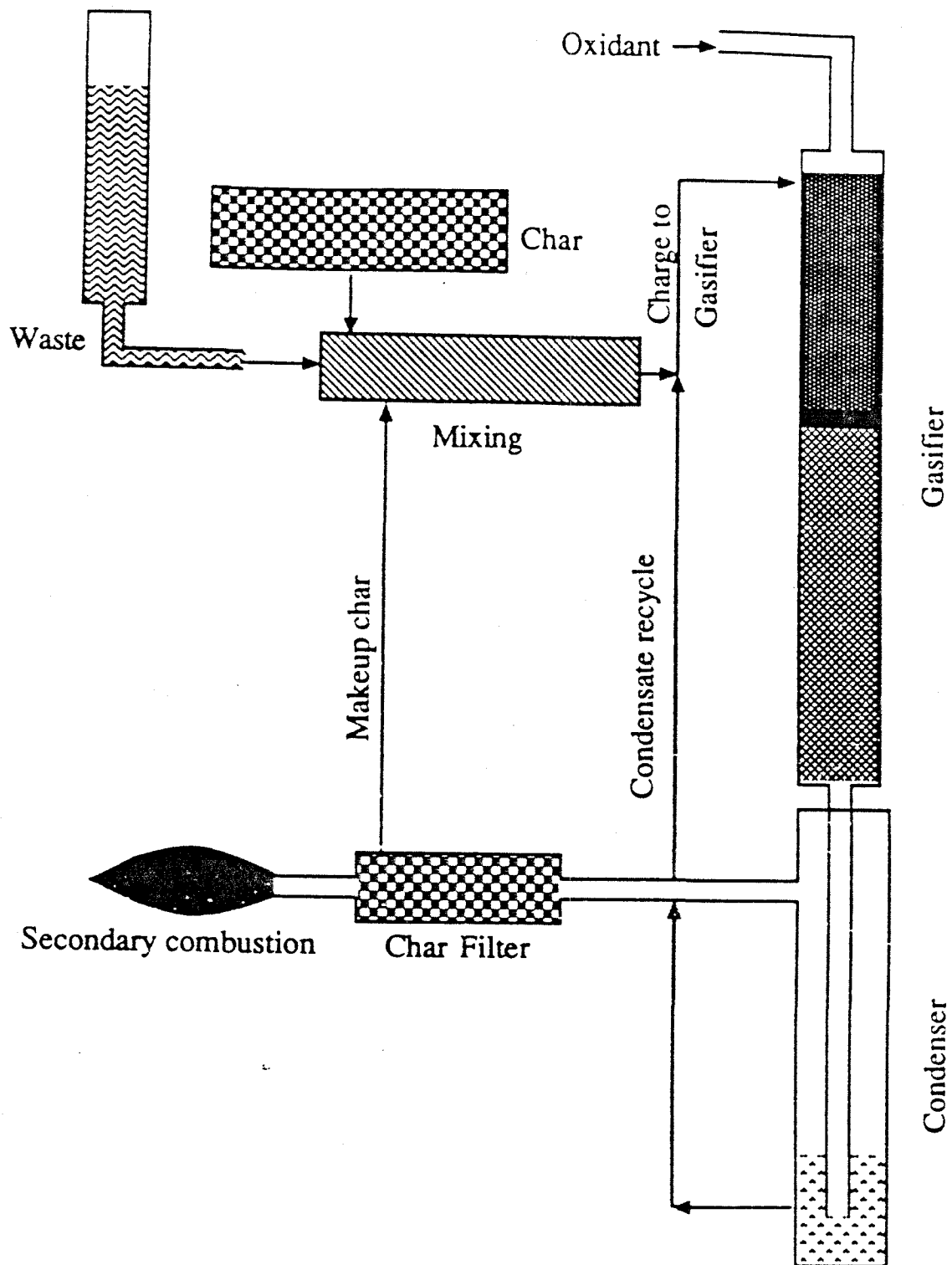
Figure 3. System for treatment of wastes by reverse-burn gasification on TRB char.

remove hazardous materials; the purified water can be discharged and the char dried and gasified. Waste sludges can be mixed directly with char or by adding enough solvents to the char/waste mixture to prevent agglomeration. The char particles act to dry these types of wastes through capillary action of the micropores in the char. Solid wastes can be macerated and mixed directly with char before being fed into the reactor. Recycled char from the char filter and recycled condensate from the condenser (Figure 3) are mixed with the feed-stock at this point.

- Gasification of the char/waste mixture in the same apparatus used for production of TRB char.

- Removal of aqueous condensate from the gas stream. This step removes most of the impurities and gasification byproducts from the combustible gas stream.

- Filtration of the gas stream through a bed of TRB char. This step removes traces of impurities not removed in the condenser.

- Combustion of the gas product. This step, which may use a catalyst for additional efficiency, burns the gas product for energy recovery, destroys any residual impurites, and enables routine achievement of >99.9999% destruction/removal of waste constituents charged to the gasifier.

- Recycle of aqueous condensate to char/waste mix. This part of the process provides makeup water for waste destruction and enables destruction of wastes in the condensate.

- Recycle of char from the filter to the char/waste mix feed to the reactor. This part of the process provides makeup char for waste destruction and enables destruction of wastes retained by the char filter.

Applications

- **Refractory Organic Waste:** Arguably the best application of reverse burn gasification is in the treatment of chemical waste sludges, particularly those containing refractory organic compounds, such as PCBs, along with heavy metals. Chemical processes in gasification effectively destroy the organic wastes and dehydrohalogenate the organohalides. The char matrix effectively retains heavy metals and (for alkaline char) HCl and other acid gases.

- **Contaminated soil:** Contaminated soil can be gasified as a mixture with char or with combustible organic material (oil or asphalt). Subsequent forward-burn gasification can be used to convert the soil to a fused material that is poorly leachable.

- **Sewage sludge:** Sewage sludge is converted to a combustible gas and a char residue by reverse-burn gasification. The gas may be burned to provide heat for drying sludge; the gasification residue consists of a char that can be recycled with additional sludge for drying and conditioning followed by gasification.

- **Mixed wastes:** Reverse-burn gasification of mixed wastes consisting of radioactive materials and organic substances destroys the organic constituents and retains the radionuclides in the char matrix. Subsequent forward-burn gasification of the solids contaminated with radionuclides can be employed to immobilize radioactive wastes in a slag matrix with a volume that may be as low as a few percent of the mixed waste feedstock.

- **Spent activated carbon regeneration:** Spent activated carbon can be regenerated by reverse-burn gasification.[8] Heavy metals are retained on the carbon, as are acid gases (HCl), to the extent that the carbon is alkaline. The sorptive properties of the carbon are restored by reverse-burn re-activation.

EXPERIMENTAL

Reagents and Apparatus. Deionized water and analytical grade chemicals were used in all applications.

Construction of Laboratory Scale Reactor. The laboratory scale batch reactor was constructed from a 2.2 cm inside diameter, 30 cm long tube composed of optically transparent Vycor® tubing to which steel fittings were bonded with heat-resistant J-B Weld® epoxy resin cement. The charge was held in the reactor by plugs of silica wool at both ends. Oxidant flow to the reactor was measured with a rotameter. Water vapor was added to the oxidant in some cases by bubbling the gas through water contained in a heated flask, the temperature of which was varied to regulate the fraction of water vapor in the oxidant.

Refractory Organic Waste

Sample train components used to sample combustible effluent gas were subjected to three consecutive rinses with acetone followed by three consecutive rinses with hexane. The aqueous condensate collected in the condenser was extracted three times with hexane, and the combined organic extracts were dried by removal of water with solid sodium sulfate. XAD resin in the resin trap was extracted with hexane in a Soxhlet extractor. The extracts and rinses from all the sampling train components except the last trap were combined to give a composite sample; the last trap was analyzed separately to ensure complete collection of analytes in the sampling train. The composite trap sample and the last trap sample were reduced to 1 mL under vacuum, and bromobenzene added as an internal standard. Residual solid materials from gasification were subjected to Soxhlet extraction with hexane, and the extract was reduced to 1 mL under vacuum.

Organic analytes in the concentrated samples were analyzed by GC-MS full scan (45-450 m/z) and quantitated with (HCB) standards. The minimum intrumental detection limit (MDL) for the GC-MS method employed was 1 ng for HCB.

Hexachlorobenzene

11

Contaminated Soil

The experimental techniques employed for gasification of contaminated soil were the same as those applied to gasification of refractory wastes above.

For collection of the metals in the gases from gasification of waste soil, traps containing a mixture of 5% HNO_3/10% H_2O_2 were used. Metals in the residue were analyzed after extraction with 0.5 N acetic acid. Volatile chloride was collected from the gas product in base traps and extracted from solids with water for analysis by ion chromatography.

Sewage sludge

Sewage sludge was collected from the anaerobic digester of the Columbia, Missouri municipal sewage treatment plant. The sludge was centrifuged to prepare a sludge cake. Dried sludge was prepared from the sludge cake by drying it in a thin layer under a stream of dry air for 48 hours.

Mixed Waste

Ion exchange resin. The organic consituent of the simulated mixed waste studied was Amberlite IRN-78, a strongly basic nuclear grade anion exchange resin in the OH form. The particle size ranges from 16-50 mesh with an effective size of 0.38-0.45 mm. The maximum moisture content is 60 %.

Technetium-99m. This radioisotope was produced from the decay of $^{99}MoO_4^{2-}$ on an activated alumina column. ^{99m}Tc is eluted from the column with normal saline solution as $^{99m}TcO_4^-$. The activity of 99mTc was counted with a well-type NaI(T1) solid scintillation detector to measure the 140.5-keV g emission.

Gasification of technetium-99m. A sample containing radioactive ^{99m}Tc as TcO_4^- loaded onto anion exchange resin was slurried with water and mixed with char in a 1:3 ratio. The resin/char mixture was air dried and charged into the reactor con-

figured so that the gas flowed upward, rather than the conventional downflow configuration shown in Figure 1. A TRB char filter was added to the column downstream from the char/resin mixture as a precautionary measure for adsorption of volatilized components. The resin/char mixture was subjected to reverse burn gasification and the activities of 1 cm^3 volumes of resin/char product, glass wool, and filter char were measured.

Spent Activated Carbon Regeneration

Activated Carbons. The granular activated carbons that were spent and regenerated were (1) Darco®, Norit Co., 20-40 mesh; Cecarbon™ GAC 40, and ChemChar TRB char, 20-60 mesh.

Spending and Reactivation of Carbon. Carbons were deaerated by boiling in water and cooling. The carbons were suspended in water and loaded over a 24-hour time period in contact with 0.11% HCB applied as a benzene solution of HCB. The solutions were removed and, after oven drying at 120°C until free flowing, the carbons were regenerated by reverse-burn gasification at an oxygen flow of 2 L/min. After removal of a 2.0 g sample for breakthrough assay with phenol, the process was repeated three times for subsequent regenerations.

Breakthrough Curve Assay. For flow-through measurement of sorptive capacity, carbons were ground to a powder and a 0.5 g portion loaded into a 3 mm inside diameter stainless steel column through which a 1000 ppm phenol solution was pumped at 0.5 mL/min with a Waters high pressure liquid chromatography pump. Ultraviolet absorbance was measured at 254 nm, and sorptive capacity calculated at the point where the plot of absorbance *vs.* volume rose abruptly from baseline.

Surface Area Measurements. Surface area measurements were performed by the nitrogen adsorption isotherm (B.E.T.) method using a Quantasorb QS-10 Surface Area Analyzer (QuantaChrome Corp., Syosset, NY, USA)

RESULTS AND DISCUSSION

Refractory Organic Waste

Hexachlorobenzene, HCB, was chosen for study as a compound representative of refractory organic wastes. It is a non-volatile, completely chlorinated hydrocarbon that is very difficult to destroy thermally and chemically. Because it is an extremely stable organochlorine compound, it is representative of refractory organic wastes, such as PCBs.

The data for HCB gasification are given in Table 1. Unreacted HCB and its gasification products were analyzed in the char residue and in the combustible product gas leaving the gasifier and penetrating into the sampling train. To calculate destruction/removal efficiency (DRE) in a manner consistent with practices applied to hazardous waste incineration, only those products penetrating to the sampling train were considered. Products that stay in the gasification reactor are not counted because they are recycled to the reactor and destroyed. The DRE for HCB from these studies is 99.99%. However, even this figure understates DRE because, in the gasification and sampling configuration employed, the 0.01%

Table 1. Gasification of Hexachlorobenzene Representative of Organohalide Sludge[1]

	Mass of analyte detected	
Analyte	In sampling train[2]	In residue[3]
HCB	4.3 µg (0.01% of original HCB)	12.5 µg (0.03% of original HCB)
PCBz[3]	32.0 ng (0.0000074% of original HCB)	300 ng (0.00069% of original HCB)
Tetra Bzs	nd (not detected)	nd
Tri Bzs	nd	nd

[1] Reverse-burn gasification of 43.0 mg hexachlorobenzene (HCB) representative of refractory organohalide wastes on 10.0 g of TRB char at an oxygen flow rate of 1.84 L/min

[2] Composite train samples. The last trap in the sample train was analyzed separately for HCB and other organohalides, the absence of which served to verify complete trapping of unreacted HCB and products of its incomplete gasification in the product gas.

[3] PCBz, tetra Bzs, and tri Bzs stand for pentchlorobenzene, tetrachlorobenzene, and trichlorobenzene, respectively.

undestroyed HCB includes HCB condensed from the gas product as an aqueous condensate, which, too, would be recycled to the gasifier in a commercial operation.

An item of major concern in conventional incineration is the production of products of incomplete combustion, PICs,[9,10] especially chlorinated dibenzofurans and dibenzodioxins.[11] An analogous concern in gasification waste treatment is possible generation of products of incomplete gasification, PIGs. Few such substances were detected in the effluents studied. Of particular significance is the complete absence of chlorinated dibenzofurans and dibenzodioxins.

Contaminated Soil

The soil studied was contaminated with hydrocarbons, PCBs, and thorium; in addition, it was spiked with zinc, lead and copper. This soil was loaded onto char and gasified with a reverse burn followed by a forward burn. Condensible materials and water were removed from the gas stream in a condenser, and the dried gas stream was filtered over TRB char. On a commercial basis both the aqueous condensate and the char from the filter would be recycled to the gasifier, so any unreacted parent material or byproducts thereof would not count against the DRE. After passing through the condenser and the char filter, the combustible gas product was burned and the combustion gases passed through a sampling train for measurement of ultimate DRE. Therefore, the sequence described above is gasifier>condenser>char filter >secondary combustion>sampling train.

The results from the gasification of contaminated soil are given in Table 2. The DRE exceeded 99.9999%. Furthermore, no chlorinated dibenzofurans or chlorinated dibenzodioxins were detected, indicating that these highly undesirable byproducts are not formed.

Fate of Metals in Contaminated Soil

For metal retention studies, lead, zinc and copper were collected from the gaseous effluent and analyzed in the residues. A blank was run in which TRB char

Table 2. Gasification of PCB-Contaminated Soil

	Analytes			
Sample	Di PCBs	TriPCBs	TetraPCBs	Total PCBs
Contaminated soil[1]	1042 μg	1042 μg	833 μg	2917 μg
Residue after gasification	0.013 ng	nd	nd	0.013 ng
Condensate after gasification	54.21 ng	55.61 ng	34.19 ng	144.0 ng
Char filter after gasification	7.5 ng	6.7 ng	5.1 ng	19.3 ng
Train after gasification	13.07 pg	33.81 pg	48.88 pg	95.76 pg

$$\text{Percent penetration of PCBs} = \frac{95.76 \times 10^{-6}\ \mu g}{2917\ \mu g} \times 100 = 3.3 \times 10^{-6}\ \text{percent}$$

$$\text{Percent DRE} = 100.0 - 3.3 \times 10^{-6} = 99.999997\ \text{percent}$$

[1] 10% moisture, gasified by a reverse burn followed by a forward burn at a constant oxidant flow of 0.824 L/min.

without added spiked metal or waste soil was subjected to a reverse burn, only. Two soil gasification runs were performed consisting of a forward burn followed by a reverse burn of 20% soil loaded onto char. One of these had metal only from the soil, whereas the second was spiked with 1000 μg of Pb, Zn, and Cu to give a concentration of each of the metals in the solids gasified of 80 ppm. The contaminated soil that was gasified contained 1.2 mg total Aroclor 1248, a commercially available PCB mixture widely used for PCB studies. The data from these runs are given in Table 3.

The minimum retention of metals in the gasification system can be calculated assuming that the level of each metal in each trap sample labelled "nd" in Table 3 is at the detection limit of the instrument. Based on these calculations, it is shown that the ChemChar Process retains greater than 98% of the Pb, and and greater than 99% of the Cu and Zn.

In examining the levels of metals extracted from the solid gasification residues, it is important to note that the method used was designed to show metals that are extractable from the gasification residue under acidic conditions which could be encountered in a landfill environment and not to give a metals balance. The presence of significant amounts of extractable zinc, lead, and copper from the residues of gasification of unspiked soils indicates the presence of these metals in the

contaminated soil. Of particular significance, however, is the retention of metals in the slag residue from the reverse-burn followed by forward-burn gasification of the

Table 3. Metal Retention in Contaminated Soil Gasification

Sample[1]	In traps			In residue (% retention of spike)		
	Zn	Pb	Cu	Zn	Pb	Cu
Blank of 10.0 g TRB char only	nd	nd	nd	nd[2]	nd[2]	nd[2]
Soil plus char, no metal spike[3]	nd	nd	nd	139	136	42
Soil plus char, metal spike[4]	nd	nd	nd	161(97.8%)[5]	193 (94.3%)	65 (97.7%)

[1] In each case data are given for a reverse burn followed by a forward burn gasification at an oxidant flow rate of 0.824 L/min, residue extracted into 0.5 N acetic acid reduced to 25 mL for extractable metals analysis.

[2] Analysis of 2.5 g ground TRB char after a reverse burn only.

[3] For 2.5 g contaminated soil on 10.0 g char, no metal spike, 2.7 g slag product analyzed for metals on residue.

[4] For 2.5 g contaminated soil on 10.0 g char, 1000 μg of each Cu, Zn, Pb metal spikes, 2.2 g slag product analyzed for metals on residue.

[5] Percent retention of spike given in parentheses. Percent retention = 100 - percent leached. For zinc, for example, if all the spiked metal had ended up in a leachable form, 1000 + 139 = 1,139 μg of zinc metal would have been measured, but only 161 μg was found. Therefore,

$$\% \text{ leached} = \frac{161 \text{ μg, spiked soil plus char} - 139 \text{ μg, unspiked soil plus char}}{1000 \text{ μg spiked}} \times 100 = 2.2\%$$

soil spiked with 1000 μg each of additional Pb, Cu, and Zn. If none of the added metal had been retained in the gasification residue, the levels of each of these metals recovered by simulated leaching conditions would have been well over 1000 μg instead of the 161, 193, and 65 μg observed for zinc, lead, and copper, respectively. The degree of leaching of the spiked metals may be viewed as the amount of metal leached after spiking compared to that leached from the residue formed from gasification of waste soil, alone. For example, adding 1000 μg of lead increases the amount of lead leached only from 136 μg to 193 μg. Therefore, according to the calculation shown in Footnote 5 of Table 3, the percent of spiked lead leached is

$$\% \text{ Pb leached} = \frac{193 \text{ μg} - 136 \text{ μg}}{1000 \text{ μg}} \times 100 = 5.7 \%$$

The degree of metal retention in the slag is significant, particularly in view of the fact that the solids were not treated in any particular manner designed to fix the metals.

Fate of Chloride

Waste soil containing PCBs was gasified and the inorganic chloride produced was collected from the gas product in base traps and extracted from the residue by water. The results for chloride recovery are given in Table 4.

Table 4. Inorganic Chloride Production

Run	Volume of gas product at STP	Chloride in Traps[1,2]	Chloride in residue + char filter[1]
1[3]	0.005 m^3	nd (not detected)	nd
2[4]	0.010 m^3	170 ng	548 µg

[1] Chloride as Cl⁻, chloride MDL = 100 parts per billion (ng/mL)
[2] No chloride found in last trap, indicating high collection efficiency
[3] 10.0 g char, no added waste, reverse burn followed by a forward burn
[4] 20% loading of waste on char, 1.23 mg Aroclor 1248 by analysis, reverse burn followed by a forward burn

The loading of 1.23 mg of Aroclor 1248 (48% chloride) onto char would yield 590 µg Cl⁻ at 100% conversion of organic chlorine to inorganic chloride. The 170 ng of chlorine emitted into is equivalent to 0.03% chlorine in the gas stream. This result, accomplished without any additional pollution control devices, is well below the U.S. EPA and RCRA incinerator regulations limit of 1% of the total amount of chloride feed.

Sewage Sludge

Sewage sludge dried to 25% water was mixed with an equal mass of TRB char and reverse-burn gasified to produce a char residue. The char residue was then mixed with an equal mass of fresh dried sewage sludge and the mixture gasified again. This procedure was repeated for a total of 7 cycles. The results are shown in Table 5.

Table 5. Gasification of Sewage Sludge

	Weights of Reactants and Products, g				Percent net conversion
Run	Sludge	Char	Residue	Water collected	of sludge to char[1]
Gasification of sludge/char mixtures					
1[2]	10.0	10.0	10.0	3.0	0
2[3]	10.0	10.0	12.0	3.0	20
3-7[3]	10.0	10.0	15.0±0.5	3.0±0.5	50
Gasification of granular dried sludge, alone					
1[4]	20.0	0	16.0	2.0	80
2[4]	20.0	0	14.0	2.0	70

[1] Percent net conversion $= \dfrac{\text{Weight of sludge - weight loss of solids during gasification}}{\text{Weight of sludge}} \times 100$

[2] Char used was TRB char prepared by gasification of subbituminous coal.

[3] Char used was char from the preceding run. For each run in sequence, a progressively lower percentage of the char was from the TRB char and a higher percentage from the sludge.

[4] Char generated gasification of the dried sludge, alone.

The gas produced by the gasification of sludge and dried by condensation of water burned very well, indicative of a high heat content fuel. In all but the first of the sequential runs, a net production of char was observed. Therefore, reverse-burn gasification converts sewage sludge to a dry, sterile, char material that can be recycled to gasify additional sludge. As indicated by the two runs for gasification of dried sludge, alone, sludge gasification can be performed without added char. However, char is desirable as a sludge conditioning agent and to promote uniform gasification. Significantly, all the char needed for these purposes can be produced from sludge. Excess char from sludge gasification is a sterile, high-heat-value material that could readily be used as a fuel.

Mixed Waste

Radionuclide retention in waste treatment was measured using radioactive technetium-99m. In addition to being a significant contaminant nuclear fission by-product, this radionuclide is a standard one used for a wide range of radiotracer and imaging studies because of its optimum half-life and radiation charcteristics.

The results obtained in the radiotracer experiment are illustrated in Figure 4, in which activity is in units of counts/min. The reactor retained all of the radioactivity detected, of which 99.9 % remained on the char/resin residue. The remaining 0.1% activity was retained in the glass wool immediately downstream from the mixture gasified and located between the char/resin column and the char filter became damp from moisture evolved during gasification. This filter became moist from the gases evolved, and the moisture probably carried with it the small amount
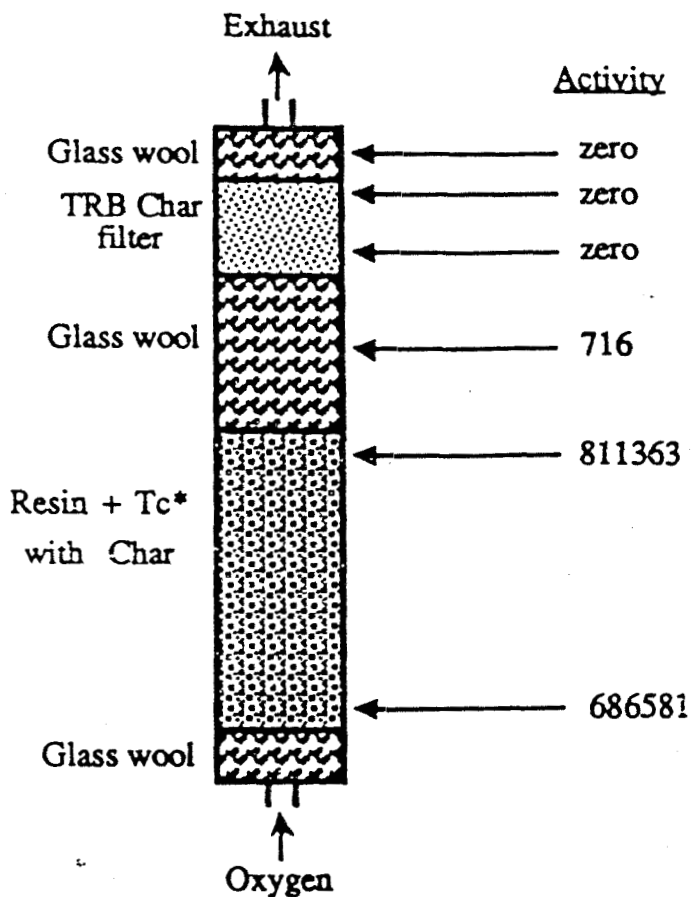

Figure 4. Retention of ^{99m}Tc in the gasification of a mixture of char and anion exchange resin laden with ^{99m}Tc. Activity is in units of counts per minute.

of activity that was found on the glass wool plug. No activity was detected in the char filter immediately downstream from the glass wool plug. These results demonstrate the superb ability of the char to retain metals while the organic portion of the waste ion exchange resin is destroyed.

Spent Activated Carbon Regeneration

Carbon regeneration data are given in Table 6. The data show that, for the most part, capacity is retained in regeneration; in the case of TRB char, it is significantly enhanced. Surface area is essentially unchanged through two successive regenerations. The physical integrity of the carbons remained intact and adequate for use in all cases through three successive regenerations. Scanning electron microscopy of CeCarbon showed that it changed from a very closed structure for the original material to a significantly more porous material with numerous surface crevices for the regenerated material. The carbon itself provided all the fuel needed for regeneration. For each regeneration cycle the mass loss of carbon was approximately 10%, which is acceptable from an economic viewpoint.

Table 6. Capacity and Surface Area of Carbons before and after Successive Regenerations[1]

	TRB Char		Darco®		Cecarbon™	
Number of regenerations	Capacity, mg/g	Surface area, m³/g	Capacity, mg/g	Surface area, m³/g	Capacity, mg/g	Surface area, m³/g
0	85.7	104	58.4	—	256	1000
1	85.7	70	204	—	181	1025
2	243	76	180	—	228	907
3	293	—	180	—	177	—

[1] All values for regenerated carbons were for carbons spent with HCB, except for surface area measurements for first and second regenerations of Cecarbon, in which the carbon was spent with toluene.

SUMMARY

One of the greater challenges facing professionals in the area of hazardous wastes is the treatment and destruction of wastes in a manner that is effective, at an acceptable cost, and in an environmentally acceptable manner, particularly from the standpoint of emissions[12] and in consideration of the production of highly toxic byproducts of treatment processes.[13] For some kinds of wastes, only the high temperatures and chemically severe conditions of thermochemical treatment processes are adequate for effective treatment. However, conventional incineration

suffers some severe disadvantages in the thermochemical treatment of wastes.[14] Gasification offers some distinct advantages over incineration, especially because it operates under reducing conditions and produces a combustible gas that can be burned very efficiently under carefully controlled conditions to destroy any remaining traces of wastes or gasification byproducts.

This paper has described the principles and applications of reverse burn gasification for the treatment of a variety of hazardous and non-hazardous substances. Reverse-burn gasification is arguably the most effective and efficient means for gasifying wastes. Occurring in a fixed bed, its unique configuration is particularly effective in dehydrohalogenating refractory organohalide compounds without producing oxygenated organohalides, particularly chlorinated dibenzodioxins and chlorinated dibenzofurans that may be produced in conventional hazardous waste incineration. The following crucial characteristics of reverse-burn gasification, particularly on a char matrix, enable an absolute minimum production of byproducts and emissions:

- Gasification occurs in a non-turbulent bed reducing production of particulate matter to minimum values.

- Because of the bed and flame front configuration, wastes must pass through the flame front, a waste-destroying "ring of fire" to leave the gasifier reactor with the product gas, thereby affording maximum exposure to waste-destroying conditions.

- Gasification is a reducing process, which prevents formation of oxidized byproducts, such as chlorinated dibenzodioxins and dibenzofurans.

- The porous activated carbon char matrix in the gasifier and in the char filter downstream very effectively retains metals, acid gases, and residual organic materials in the product (even metallic mercury vaporized in the gasifier is removed completely by the cold downstream char filter.[5]

This paper has summarized the uses of reverse-burn gasification for several important waste treatment applications. Refractory organohalide wastes were destroyed to an extent of at least 99.9999% without production of undesirable byproducts, release of metal contaminants, or evolution of significant amounts of hydrogen chloride. Destruction of wastes on contaminated soil was demonstrated. Sewage sludge was gasified with generation of more char used for sludge conditioning than was consumed. The organic constituents of mixed wastes containing both organic substances and radioactive materials were destroyed with complete retention of radionuclides, which can be incorporated into a non-leachable slag with about 5 percent of the volume of the original waste. In addition, spent activated carbon was regenerated and re-activated by reverse-burn gasification without unacceptable loss of mass, sorptive capacity, or physical integrity.

ACKNOWLEDGEMENTS

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95% volume reduction

Classified as a Subpart X Unit   "Thermal detoxifier" in ADA Oklahoma

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